# AEROSPACE MATERIALS FOR EXTREME ENVIRONMENTS

**Date: 7 March 2013**

**Dr. Ali Sayir**

**Program Officer**

**AFOSR/RTD**

**Air Force Research Laboratory**

***Integrity ★ Service ★ Excellence***

# Report Documentation Page

*Form Approved*
*OMB No. 0704-0188*



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|---|---|---|
| 1. REPORT DATE<br>**07 MAR 2013** | 2. REPORT TYPE | 3. DATES COVERED<br>**00-00-2013 to 00-00-2013** |

| | |
|---|---|
| 4. TITLE AND SUBTITLE<br>**Aerospace Materials for Extreme Environments** | 5a. CONTRACT NUMBER |
| | 5b. GRANT NUMBER |
| | 5c. PROGRAM ELEMENT NUMBER |
| 6. AUTHOR(S) | 5d. PROJECT NUMBER |
| | 5e. TASK NUMBER |
| | 5f. WORK UNIT NUMBER |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>**Air Force Office of Scientific Research ,AFOSR/RTD,875 N. Randolph,Arlington,VA,22203** | 8. PERFORMING ORGANIZATION REPORT NUMBER |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | 10. SPONSOR/MONITOR’S ACRONYM(S) |
| | 11. SPONSOR/MONITOR’S REPORT NUMBER(S) |

12. DISTRIBUTION/AVAILABILITY STATEMENT
**Approved for public release; distribution unlimited**

13. SUPPLEMENTARY NOTES
**Presented at the AFOSR Spring Review 2013, 4-8 March, Arlington, VA.**

14. ABSTRACT

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT<br>**unclassified** | b. ABSTRACT<br>**unclassified** | c. THIS PAGE<br>**unclassified** | **Same as Report (SAR)** | **28** | |

**Standard Form 298 (Rev. 8-98)**
Prescribed by ANSI Std Z39-18

**NAME:** AEROSPACE MATERIALS FOR EXTREME ENVIRONMENTS

**BRIEF DESCRIPTION OF PORTFOLIO:**
To provide the fundamental knowledge required to enable revolutionary advances in future Air Force technologies through the discovery and characterization of materials that can withstand extreme environments.

**LIST SUB-AREAS IN PORTFOLIO:**

- Theoretical and computational tools that aid in the discovery of new materials.
  - **Ceramics**
  - **Metals**
  - **Hybrids (including composites)**
- Mathematics to quantify the microstructure to Predictive materials Science
- Physics and chemistry of materials in highly stressed environments
- Experimental and computational tools to address the complexity of combined external fields at extreme environments.

# OUTLINE

## I. Predictive Materials Science

**Bulk Metallic Glasses**

Carbides (SiC, TaC, $Ta_4C$)

Textile Based Hybrid Composite

## II. Materials Far from Equilibrium

Micro-Architectured Surfaces

Surface Catalysis at Extreme Environment

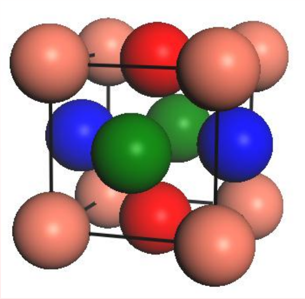
## III. Challenges, Motivations and New initiatives.

# "The Dream:" Computational Material Design

W. Windl (OSU), K. Flores (WASHINGTON U. ), D. Hoffmann (CALTECH), E. Marquis (U. MICHIGAN

Computer

Pick a set of structures & compositions



Calculate their properties

"Optimal?"

No

Improve structure/composition

Yes

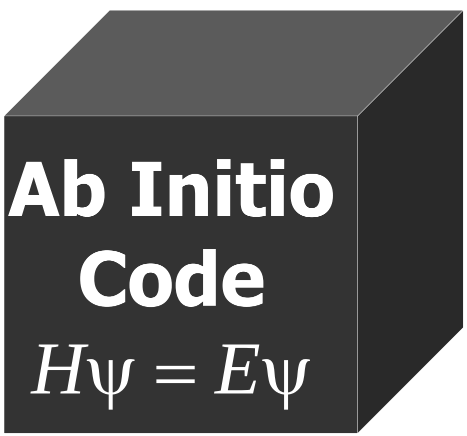
Lab or Fab

Experimental fabrication & testing

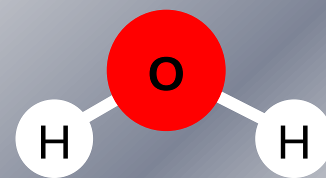
# Ab-Initio Calculations

W. Windl (OSU), K. Flores (WASHINGTON U. ), D. Hoffmann (CALTECH), E. Marquis (U. MICHIGAN

## Input:

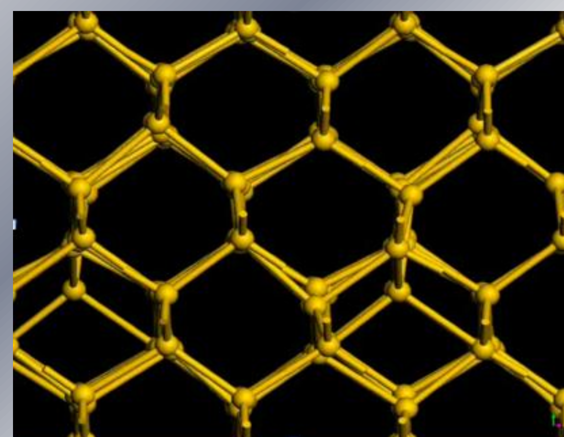



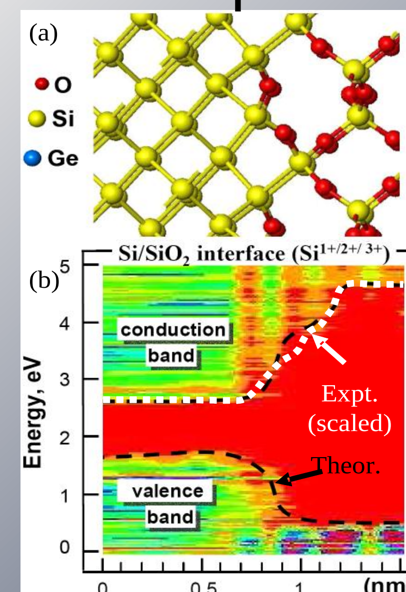

## Output:




Structure,
Energy

Band structure
EELS spectra

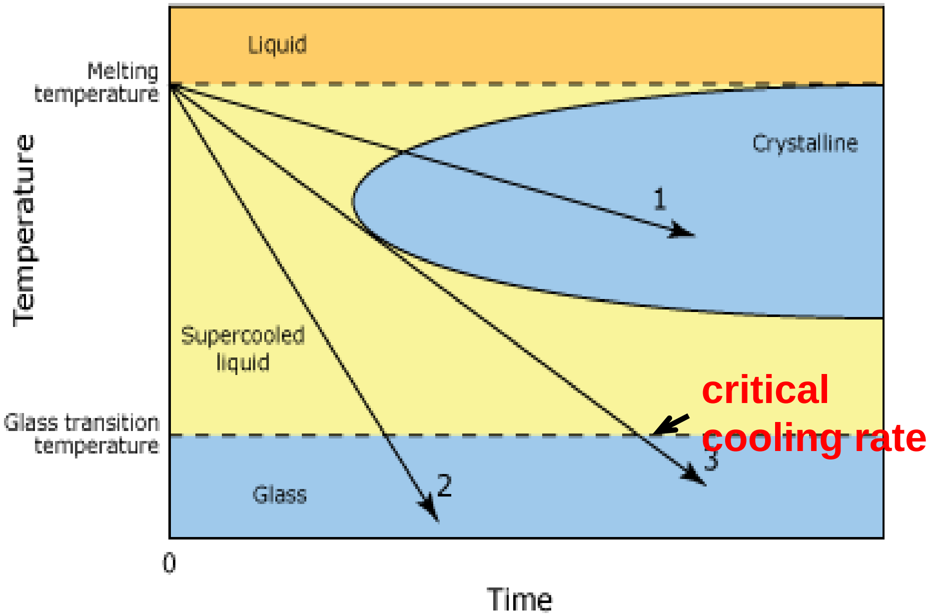


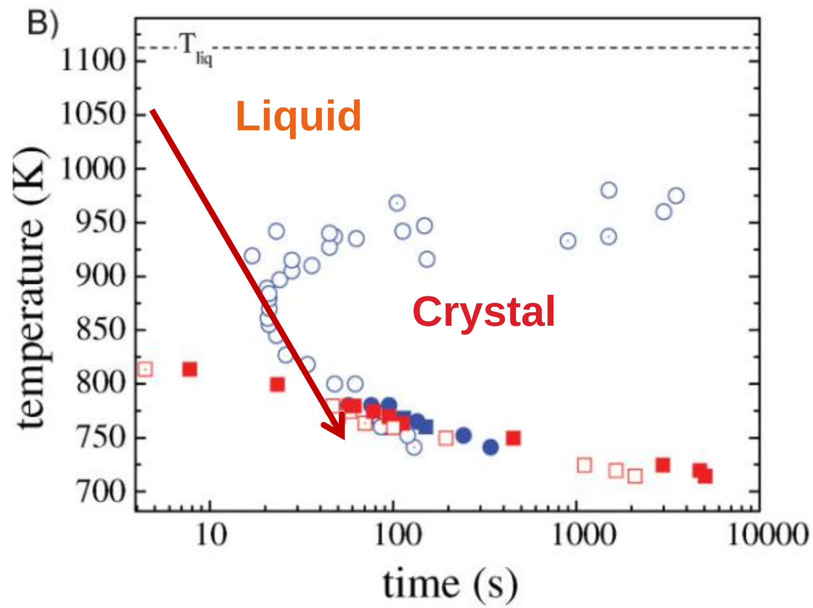



Kinetic parameters
Thermal properties
Mechanical prop’s

# Calculating Glass-Forming Ability

W. Windl (OSU), K. Flores (WASHINGTON U. ), D. Hoffmann (CALTECH), E. Marquis (U. MICHIGAN




Crystallization inhibitors:

1. Driving Force: Icosahedra
2. Kinetics: Viscosity (fragility)

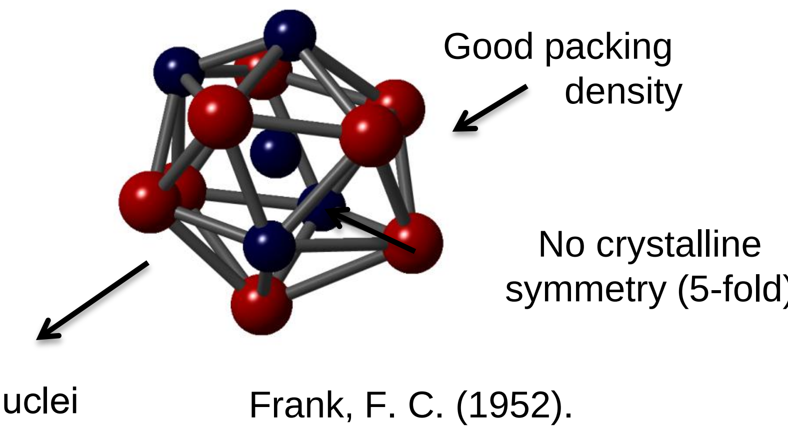
Direct Measurement:

Critical Cooling Rate

–Not computationally feasible

–Real time: 1 ms

–20 CPUs: 200 Years



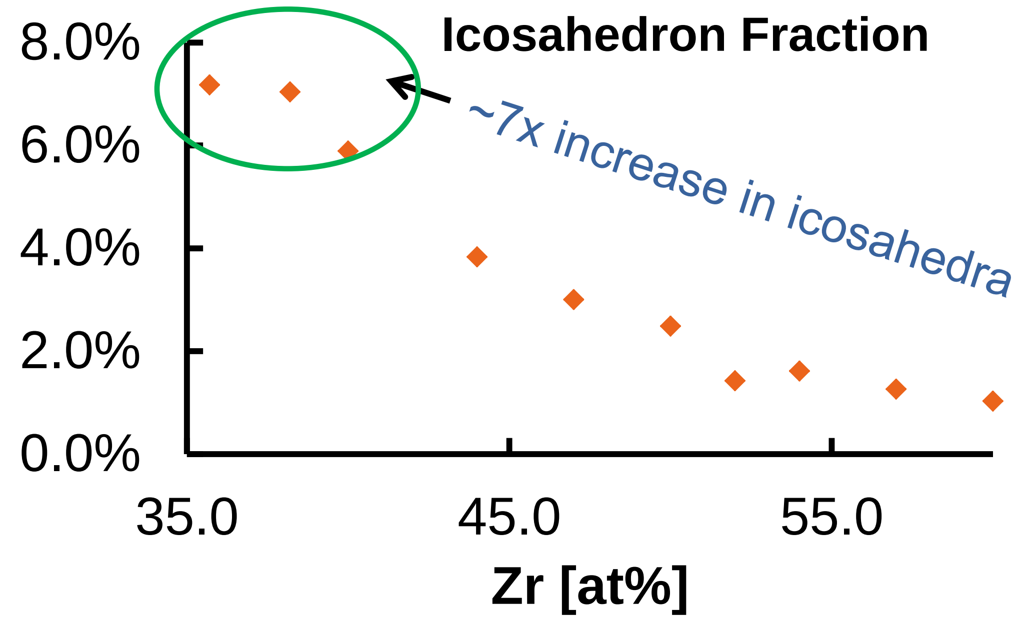

Frank, F. C. (1952).

# Interatomic Potentials

W. Windl (OSU), K. Flores (WASHINGTON U. ), D. Hoffmann (CALTECH), E. Marquis (U. MICHIGAN

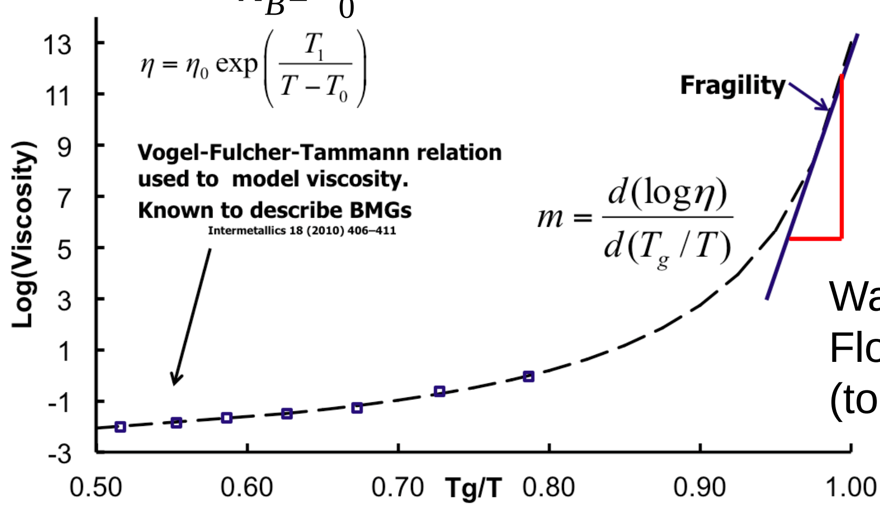
| | Ag | Al | Au | Be | Ce | Co | Cu | La | Mg | Nb | Ni | Ta | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 9.094 | | | | | | | | | | | | |
| Au | 12.056 | 6.060 | | | | | | | | | | | |
| Be | 0.710 | 1.067 | 0.509 | | | | | | | | | | |
| Ce | 4.407 | 2.196 | 3.590 | 1.246 | | | | | | | | | |
| Co | 5.400 | 1.264 | 5.946 | 0.509 | 1.657 | | | | | | | | |
| Cu | 3.049 | 3.984 | 7.424 | 0.579 | 2.045 | 4.814 | | | | | | | |
| La | 2.559 | 3.280 | 1.935 | 0.716 | 1.827 | 1.345 | 1.887 | | | | | | |
| Mg | 1.021 | 1.536 | 0.552 | 1.386 | 0.807 | 0.900 | 1.861 | 0.746 | | | | | |
| Nb | 0.694 | 1.213 | 1.041 | 0.667 | 6.288 | 2.122 | 0.611 | 2.674 | 0.194 | | | | |
| Ni | 6.836 | 4.069 | 5.339 | 0.494 | 1.812 | 7.348 | 6.123 | 2.425 | 1.129 | 5.539 | | | |
| Ta | 2.400 | 1.138 | 2.250 | 0.432 | 1.599 | 2.288 | 1.457 | 4.563 | 1.408 | 2.400 | 3.114 | | |
| Ti | 5.334 | 1.945 | 2.925 | 1.181 | 2.924 | 3.641 | 2.740 | 3.794 | 0.539 | 2.908 | 1.526 | 2.152 | |
| Zr | 2.721 | 1.500 | 2.403 | 0.924 | 3.840 | 3.089 | 3.286 | 3.851 | 3.618 | 2.371 | 1.790 | 2.225 | 8.558 |

atomistics.osu.edu

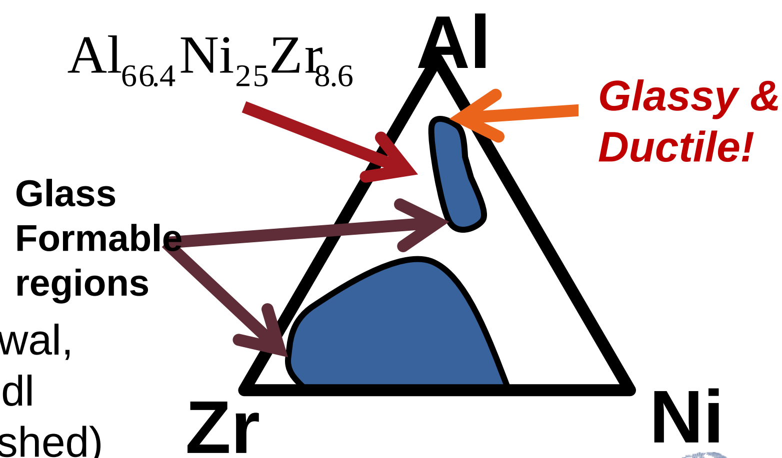


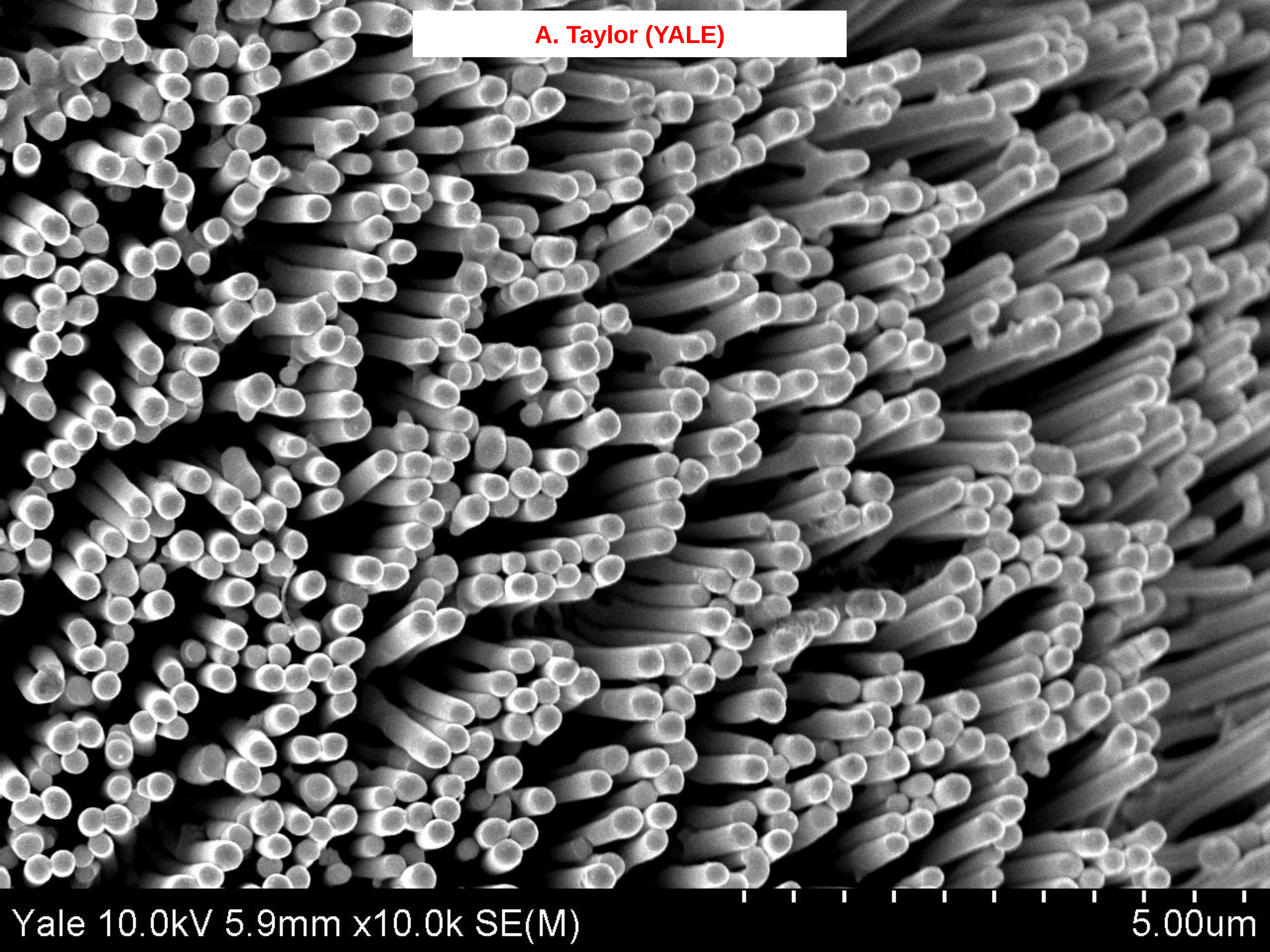

- **Chosen Method: Green-Kubo**

$$\eta = \lim_{t\to\infty} \frac{V}{k_B T} \int_0^t \left\langle P_{\alpha\beta}(t_0+s) P_{\alpha\beta}(t_0) \right\rangle ds$$




Ward, Agrawal, Flores, Windl (to be published)




A. Taylor (YALE)
Yale 10.0kV 5.9mm x10.0k SE(M)
5.00um

# OUTLINE

## I. Predictive Materials Science

Bulk Metallic Glasses

**Carbides (SiC, TaC, $Ta_4C$)**

Textile Based Hybrid Composite

## II. Materials Far from Equilibrium

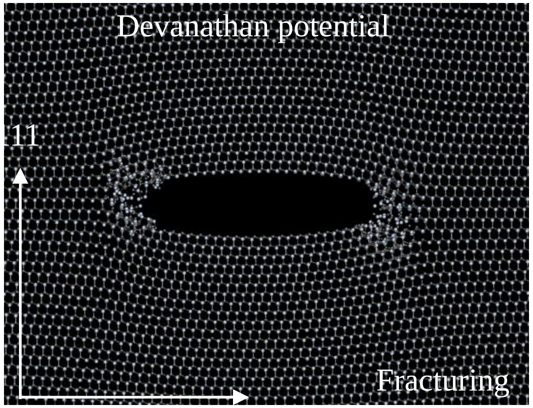
Micro-Architectured Surfaces

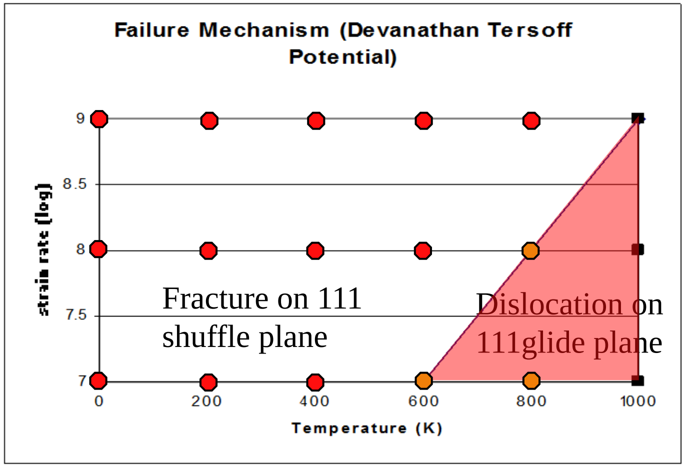
Surface Catalysis at Extreme Environment

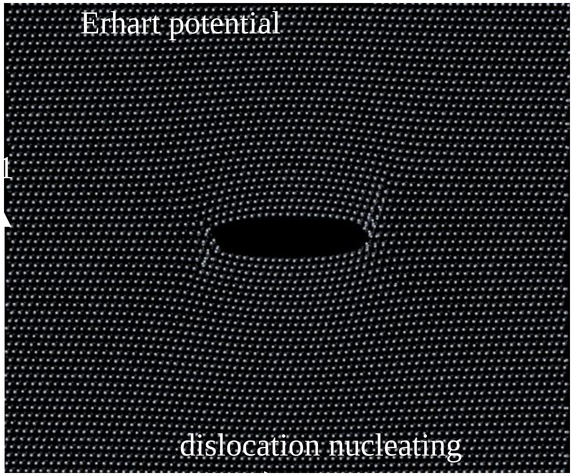
## III. Challenges, Motivations and New initiatives.

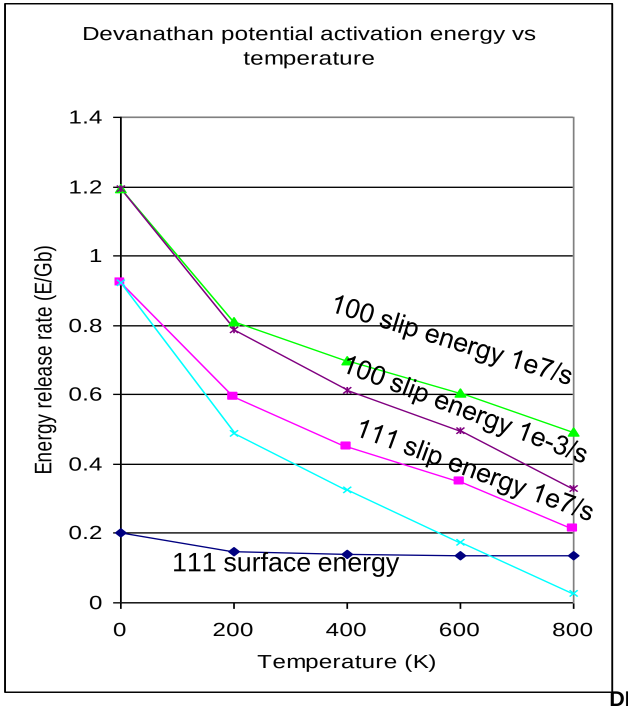
# Direct MD prediction compared to fracture and dislocation nucleation models for SiC

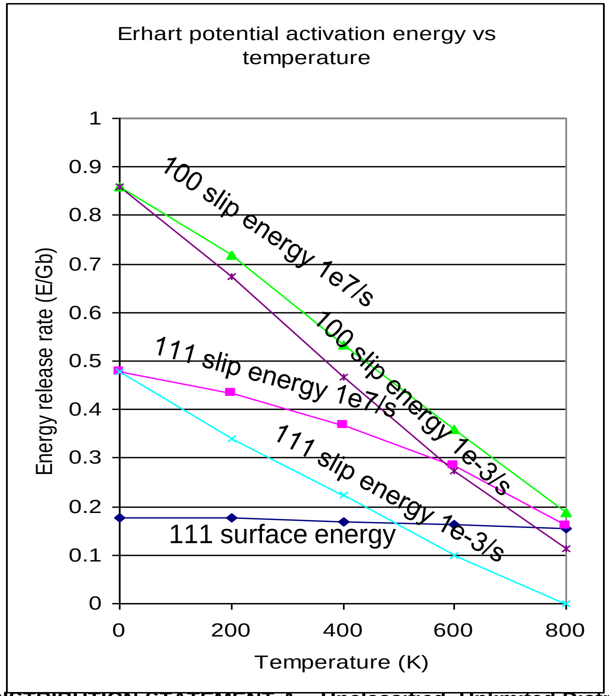
D. Warner (CORNELL U.)



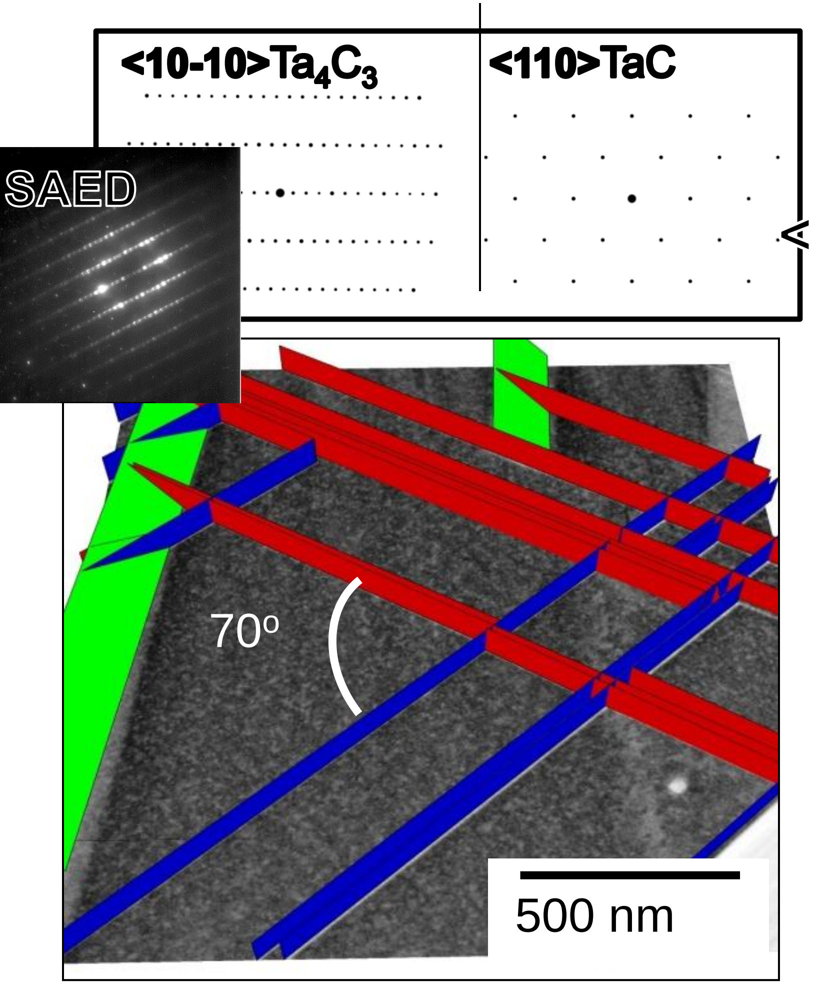



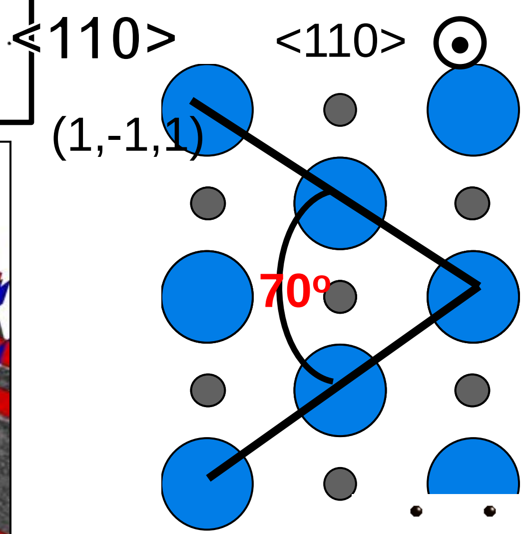

- Activation energy predicted by the continuum model
- Elastic constants(T) + surface energies(T) + unstable stacking fault energies(T) +

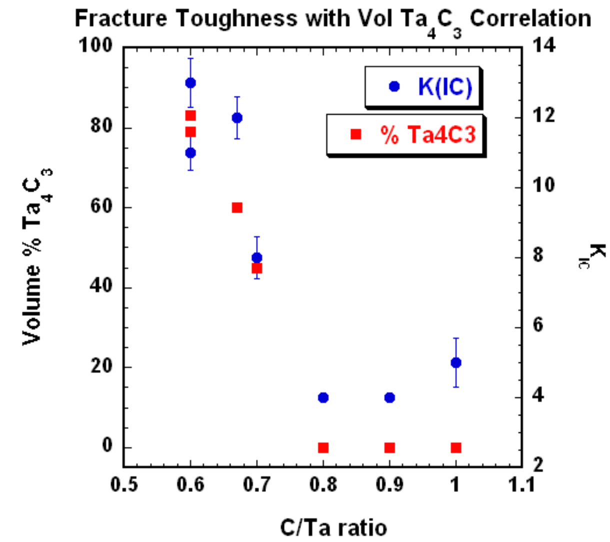
$$\frac{Q_{3D}}{k_B T} = \ln\left(\frac{k_B T N \omega_0}{-\dot{K}_I \dfrac{dQ_{3D}}{dK_I}}\right)$$

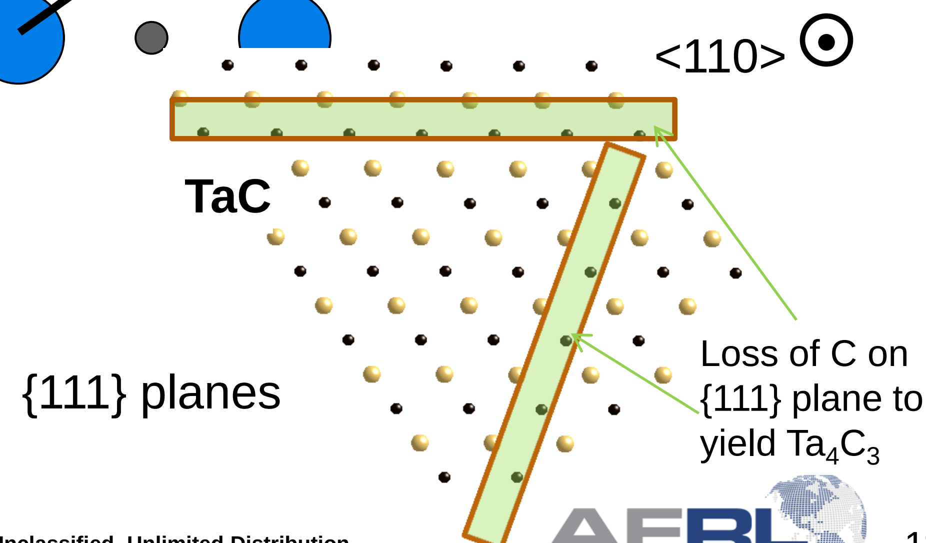
# Orientation Relationship of TaC and $Ta_4C_3$ phase

G. Thompson (U. ALABAMA)



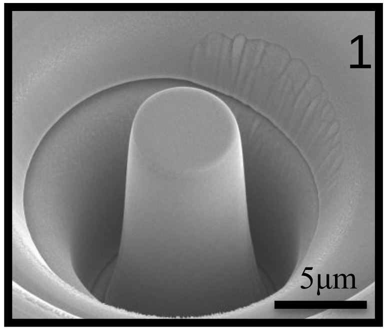



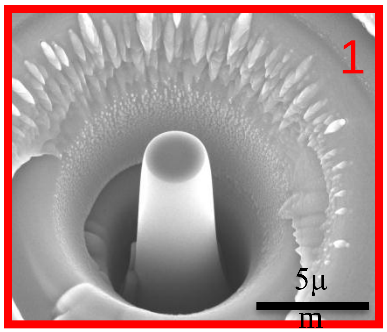



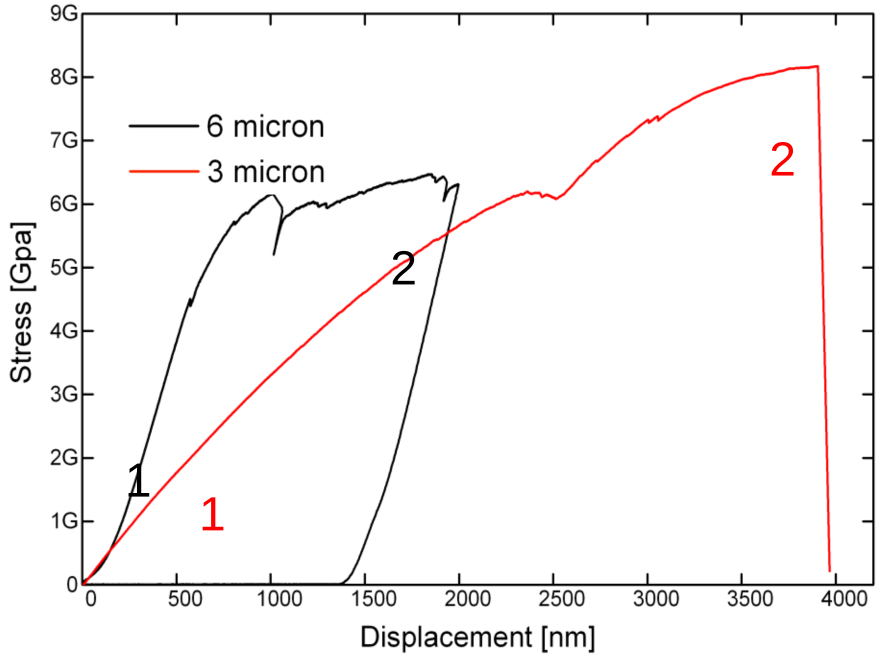

TaC FCC-like structure yields **FOUR {111} variants** – leads to equivalent precipitation habit planes for $Ta_4C_3$ -criss-cross pattern morphology of laths

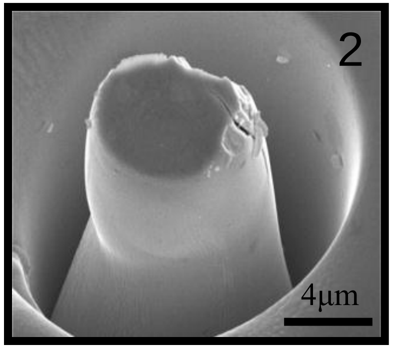
# Unsolved Problem: Scale Effect ZrC(001)

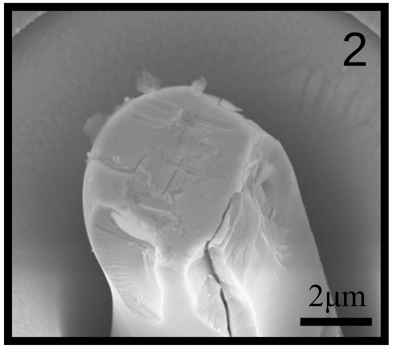
S. Kodambaka (UCLA)

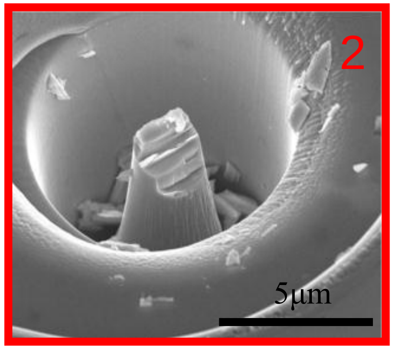



- Deviation from linearity
- Pop-in or displacement bursts, buckling, cracking
- Max CRSS on {111} planes
- Plastic flow due to formation of slip bands
- Shearing and cracking rather than catastrophic fracture specially in 6μm pillars

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# National Hypersonic Science Center

D. Marshall, B. Cox (TELEDYNE), F. Zok (UC SB), B. Fahrenholtz (MST), P. Kroll (UT AUSTIN), Q. YANG (U. MIAMI), R. RITCHIE (UC BERKELEY)

- Highly integrated research program: graduate students & post docs
- 35 journal publications; 23 plenary/keynote presentations at international conferences (including Mueller award lecture at ICACC'12, 4 lectures at 2012 Ceramics Gordon Conference); 12 conference proceedings; 25 other conference papers
- Active collaborations with 10 universities.
- Sharing of data & modeling with AFRL, Army, NASA, Rolls Royce
- Organized International Summer School on Materials for Hypersonics, UCSB, Aug. 2011. Organized International workshop on high-temperature ceramic composites, Boulder CO June 12-15 2012; www.engineceramics.org

www.nhsc-ms.org

National Hypersonic Science Center Materials and Structures

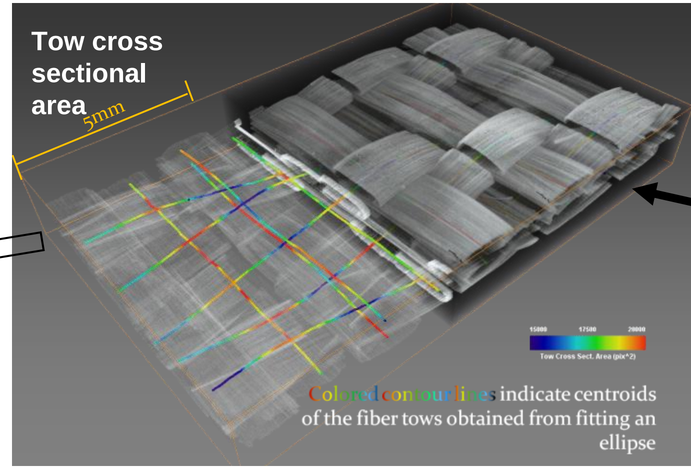
TELEDYNE SCIENTIFIC COMPANY

# 3-D Microstructural Characterization and Geometry Generator

D. Marshall, B. Cox (TELEDYNE), F. Zok (UC SB), Q. YANG (U. MIAMI), R. RITCHIE (UC BERKELEY)

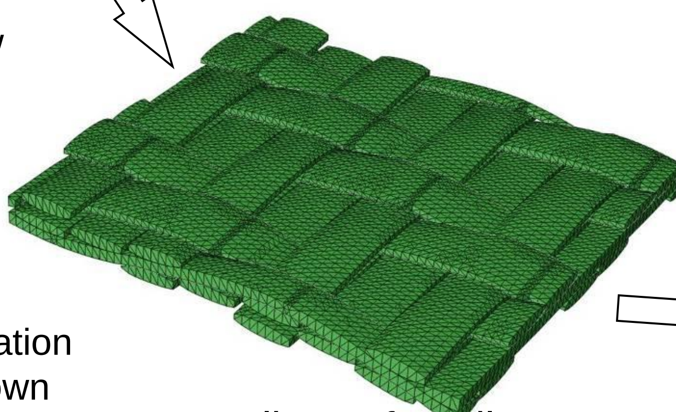
*Statistical description of geometry*

Tow paths
Cross-sectional areas
Orientation of cross section
Deviations from mean
Correlation lengths




3-D image of C-SiC composite

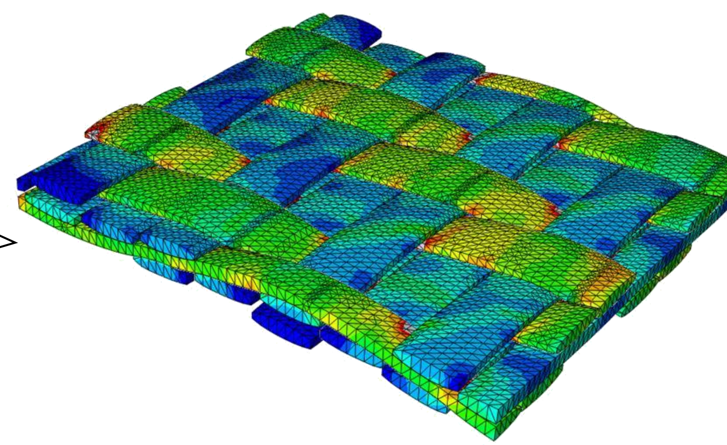
analogue of Markov chain method for tow axis coordinates $\Rightarrow$ stochastic irregular elliptical cylinder for each tow



problem: interpenetration
solution: enforce known topology of textile

create replicas of textile reinforcement with same statistics as those measured

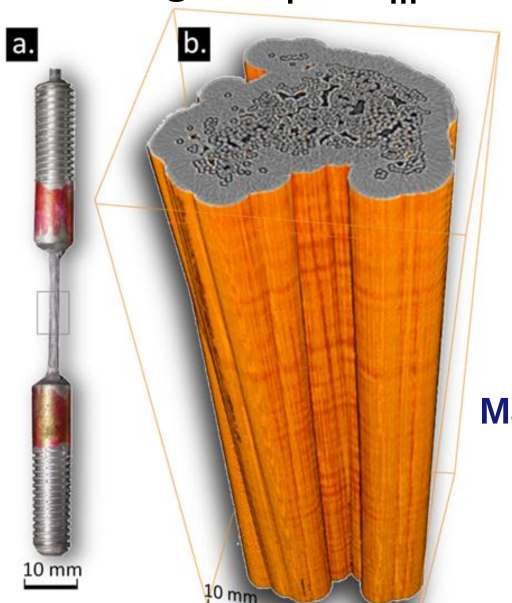
computational mesh from geometric model



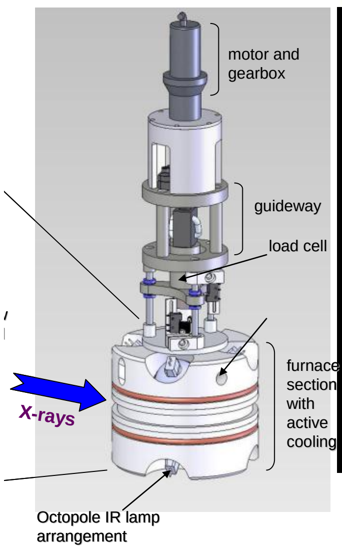
# In-Situ 3D Tomography at 1750 C

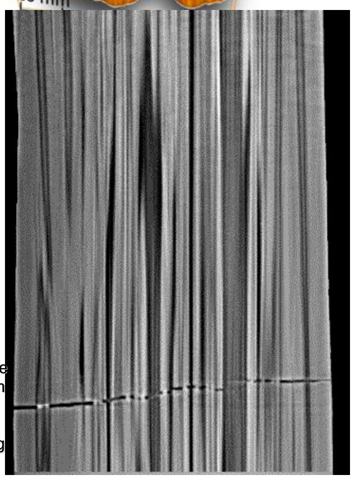
R. Ritchie (UC BERKELEY)

## In-situ testing $SiC_f/SiC_m$ at 25˚C



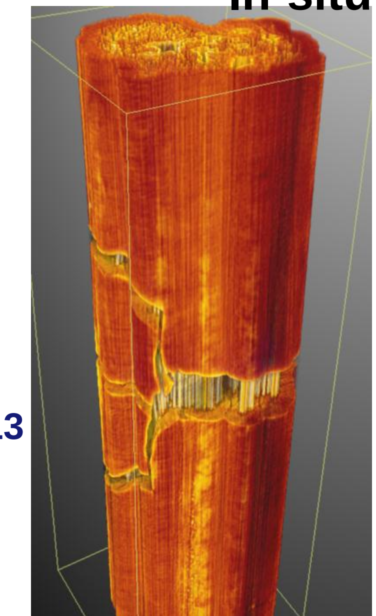

Nature of Materials 2013

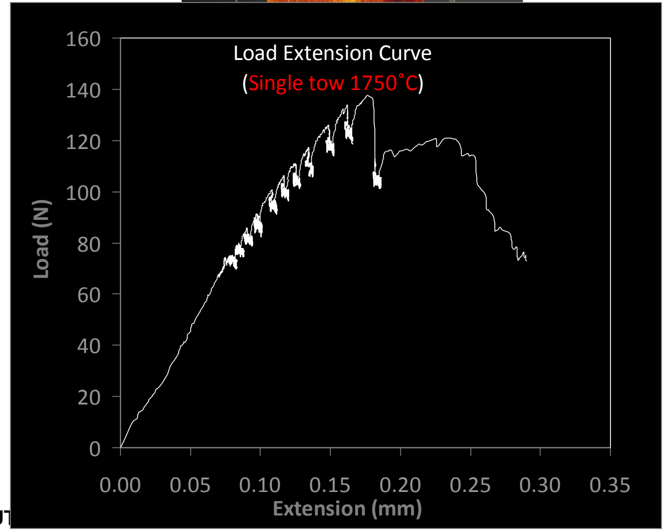


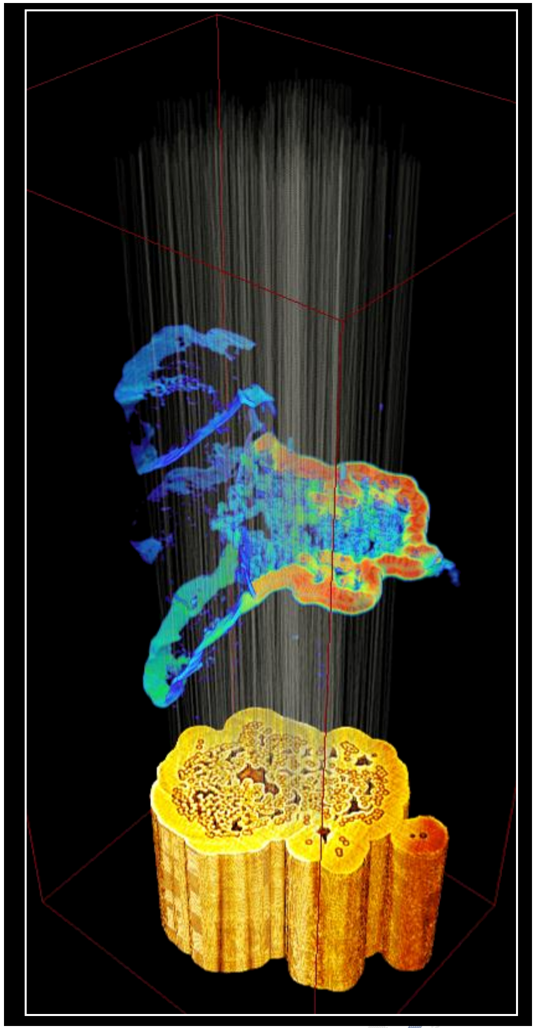



127 N, 25 $^oC$

## In-situ testing $SiC_f/SiC_m$ at 1750˚C

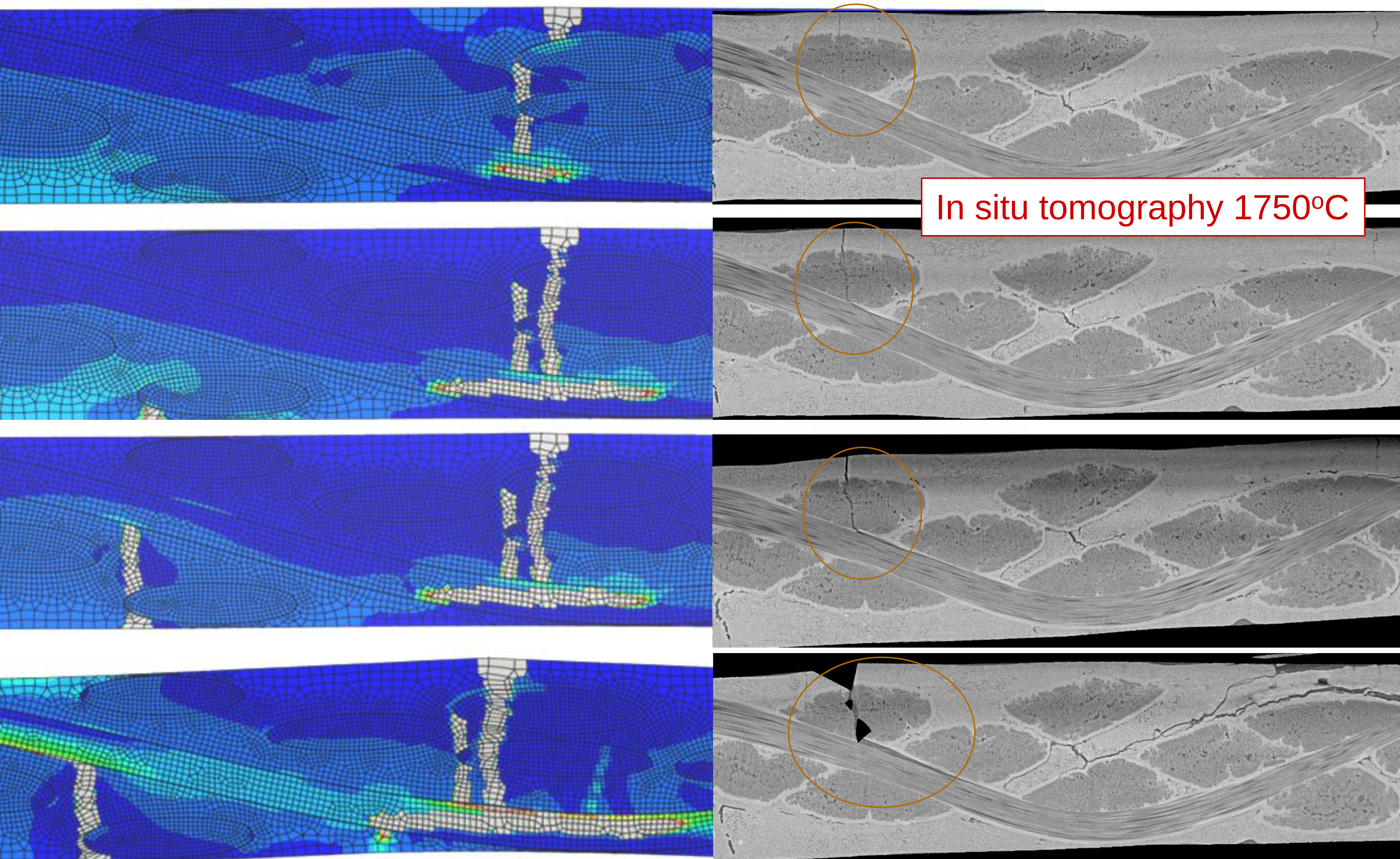




# Comparison of Simulation and in-situ Tomography

D. Marshall, B. Cox (TELEDYNE), F. Zok (UCSB), Q. Yang (U. MIAMI), R. Ritchie (UC BERKELEY)



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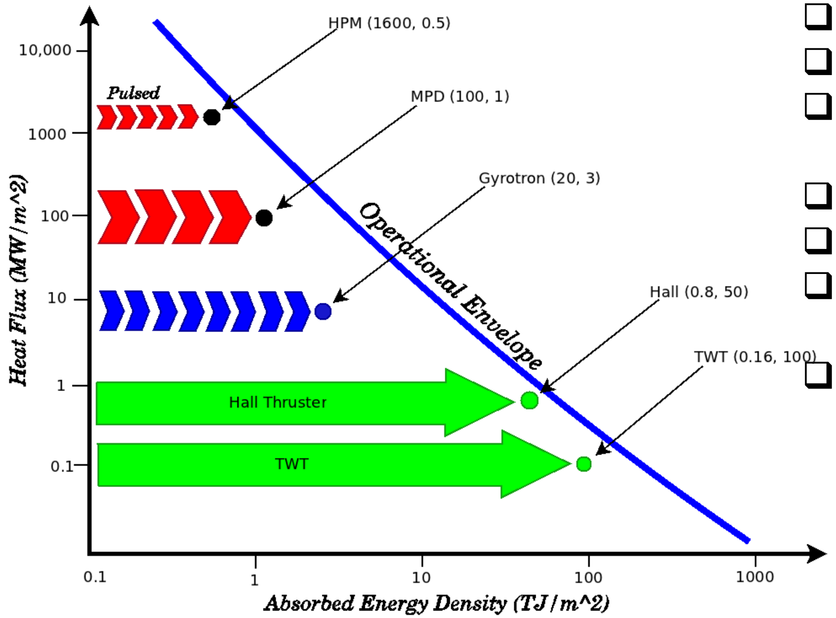
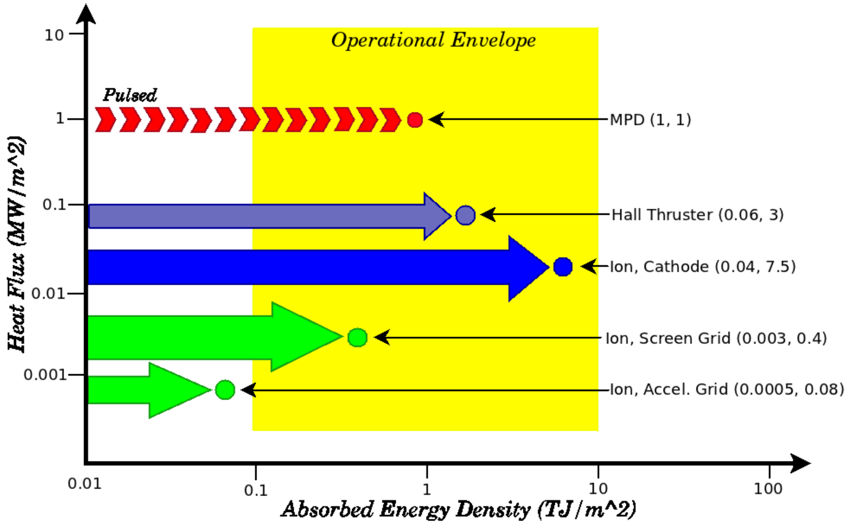
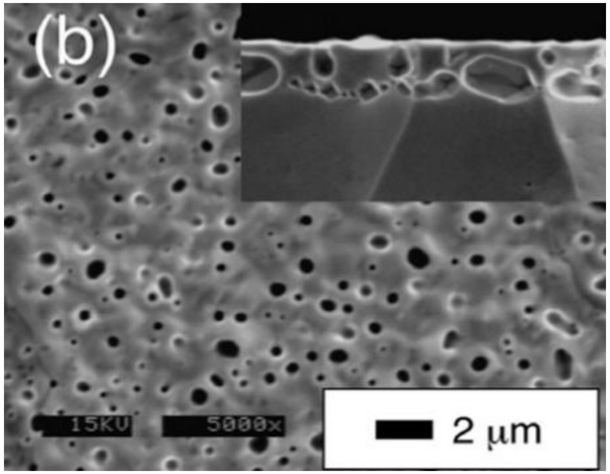
# Materials Far from Equilibrium: Micro-Architectured Surfaces

N. Ghoniem / UCLA




- Plasma Erosion & Modeling (Wirz - UCLA).
- Plasma Source Development (Goebel – JPL/UCLA)
- Secondary Electron Emission & Plasma Modeling (Raitses, Kaganovich - PPPL).
- Materials Characterization (Thompson - UA).
- High Heat Flux Testing (Ghoniem - UCLA).
- Manufacturing of Micro-architectured Materials (Williams - ULTRAMET).
- Multiscale Modeling of Material Damage (Ghoniem - UCLA).

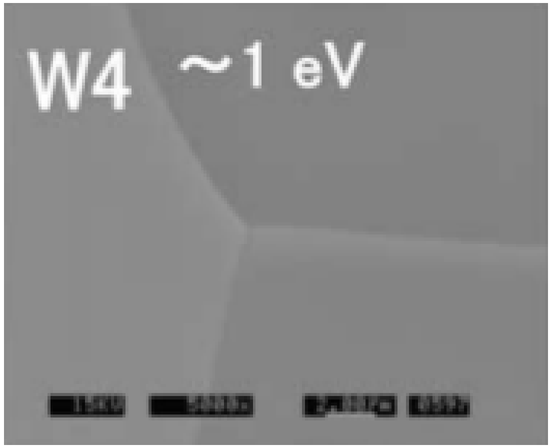


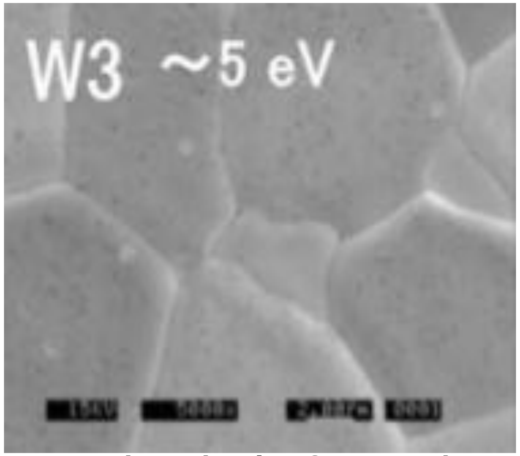

Hole formation [1994(MJ/m$^2$), 0.2 (MW/m$^2$)]

# Damage for Heat flux < 1 MW/m$^2$

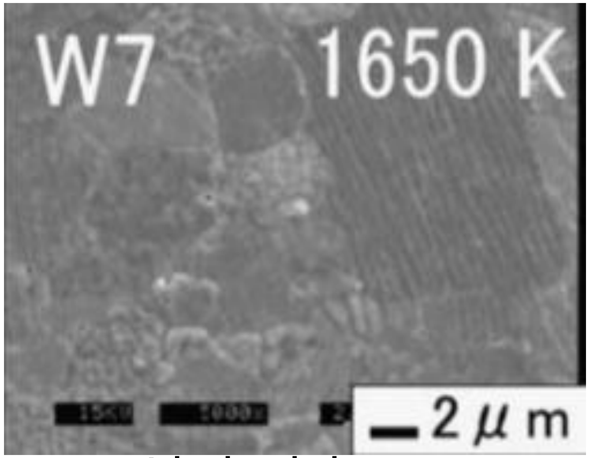
N. Ghoniem (UCLA), Y. Raitses and I. Kaganovich (PRINCETON),
G. Thompson (U. ALABAMA), B. Williams (ULTRAMET)



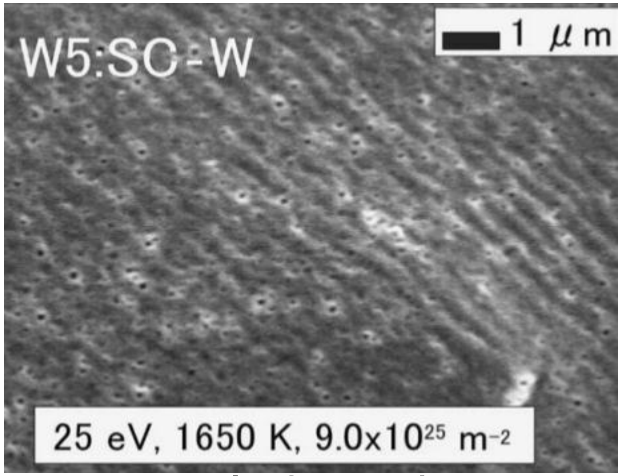

No damage
[128(MJ/m$^2$),0.02 (MW/m$^2$)]



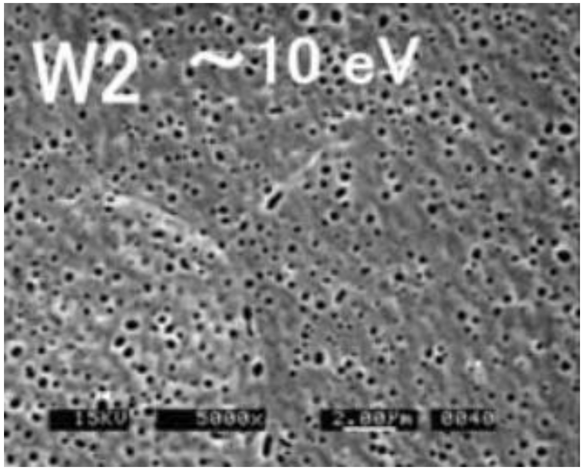

Fine hole formation
[641(MJ/m$^2$),0.2 (MW/m$^2$)]



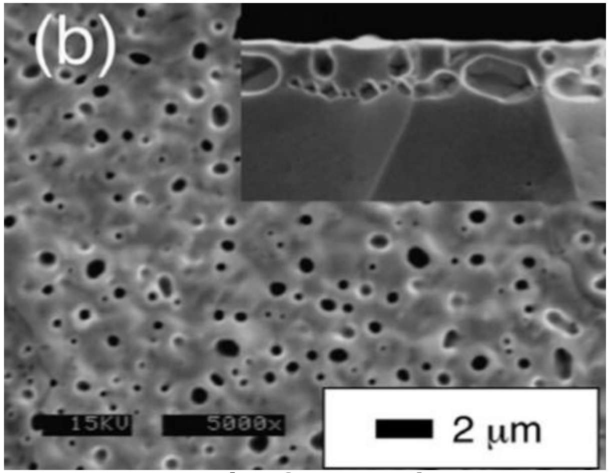

Limited damage
[721(MJ/m$^2$),0.4 (MW/m$^2$)]




Hole formation
[360 (MJ/m$^2$),0.2 (MW/m$^2$)]



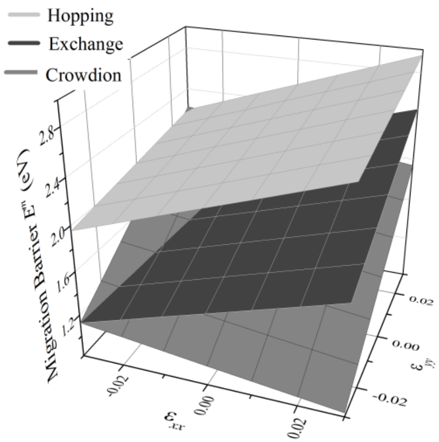

Hole formation
[1441(MJ/m$^2$),0.2 (MW/m$^2$)]



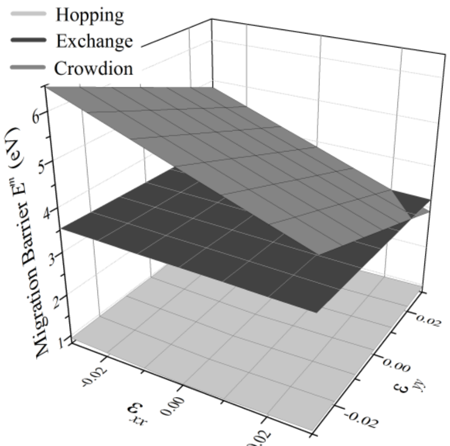

Hole formation
[1994(MJ/m$^2$),0.2 (MW/m$^2$)]

# Atomistic Simulations of Surface Defects in W under Plasma Bombardment

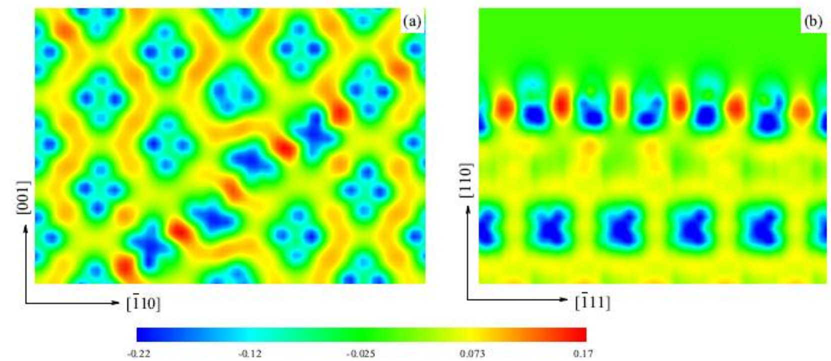
N. Ghoniem (UCLA)




(001)



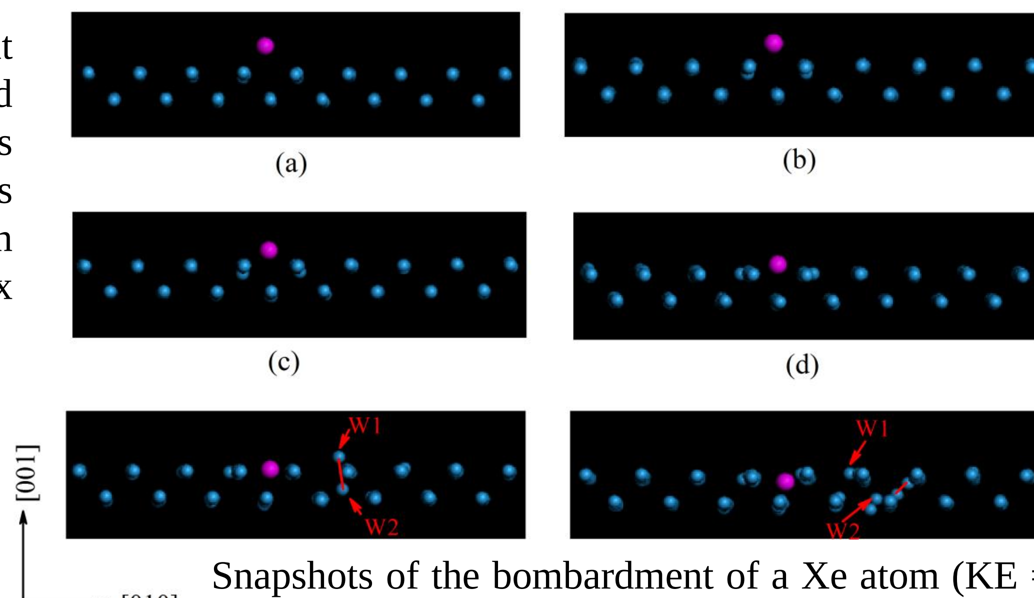

(110)




ρ(r) of surface crowdion indicates the high mobility and strong anistropy of its movement.

Hopping of the adatom is the dominant mechanism on (110) surface. The formation and the movement of surface crowdions contributes mostly on (001) surface. Exchange mechanism is also important on (001) surface, biaxial strain can manipulate the relative contribution of Path-Ex and Path-Crow.

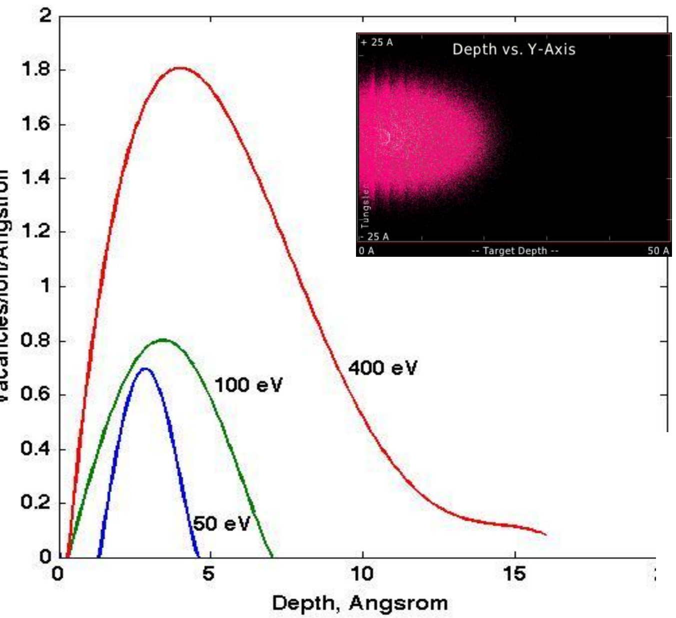
MD simulation indicates that the bombardment of a Xe atom induces ballistic diffusion of W atoms (W1 in the graph) and causes the formation and evolution of crowdions near the surface.

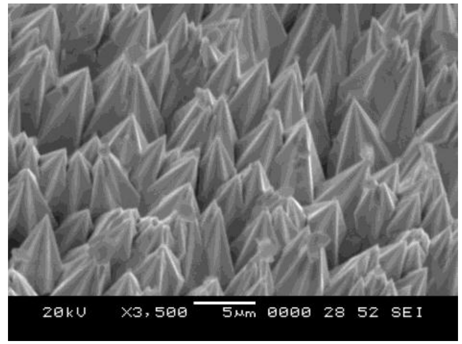



Snapshots of the bombardment of a Xe atom (KE = 100 eV) on W(001) surface at $T$ = 200 K.

# Vacancy Production in Surface Layers Leads to Surface Instabilities

N. Ghoniem (UCLA)



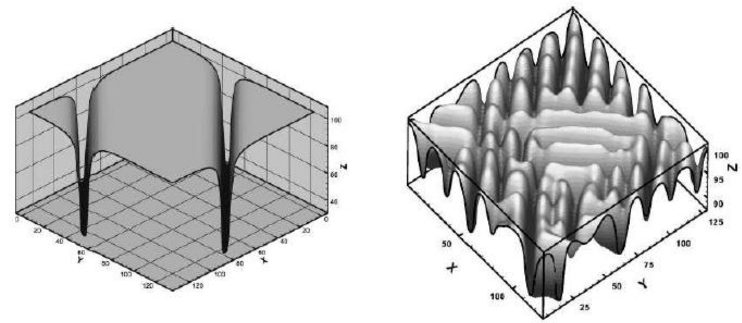
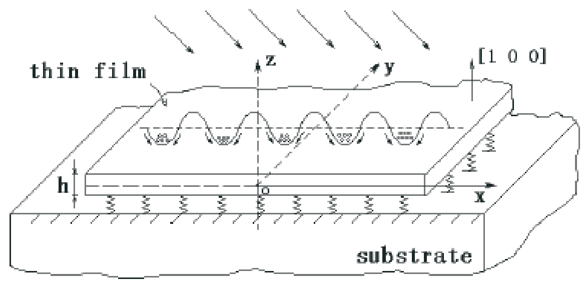



FIG. 14.20. Groove patterns seen under a biaxial stress state in which one side is under tension and the other is under compression [713].




D. Walgraef, N.M. Ghoniem, and J. Lauzeral. Deformation patterns in thin films under uniform laser irradiation. *Phys.Rev.*, B 56:15361–15377, 1997.

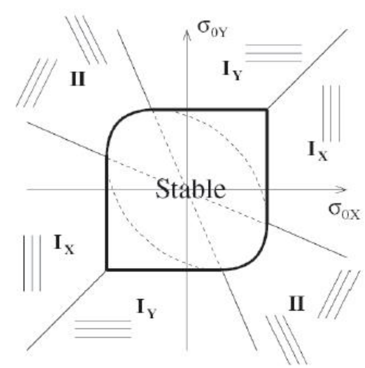



FIG. 14.21. ... pattern selection in biaxiall

$$\nabla.\mathrm{U} = -zm\triangle\xi\,,$$

$$\partial_t^2\xi + \frac{c^2h^2}{12}\Delta^2\xi - \frac{c^2}{2}\sigma_{ij}\partial_{ij}^2\xi + \frac{\theta_v}{\rho h}(C_+ - C_-) = 0\,,$$

$$\partial_t C = D_\perp \partial_{zz}^2 C + D_\parallel \triangle C - \frac{C}{\tau} + \boldsymbol{\nabla}\frac{\theta_v D_\parallel C}{kT}\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{U}) + \nabla_z\frac{\theta_v D_\perp C}{kT}\nabla_z(\boldsymbol{\nabla}\cdot\mathbf{U}) + g\exp[-\frac{E_f}{kT}](1+\theta_v\boldsymbol{\nabla}\cdot\mathbf{U})$$

Jerome Paret. Long-time dynamics of the three-dimensional biaxial grinfeld instability. *Physical Review E*, 72:01105–1–5, 2005.

# OUTLINE

## I. Predictive Materials Science

Bulk Metallic Glasses

Carbides (SiC, TaC, Ta4C)

Textile Based Hybrid Composite

## II. Materials Far from Equilibrium

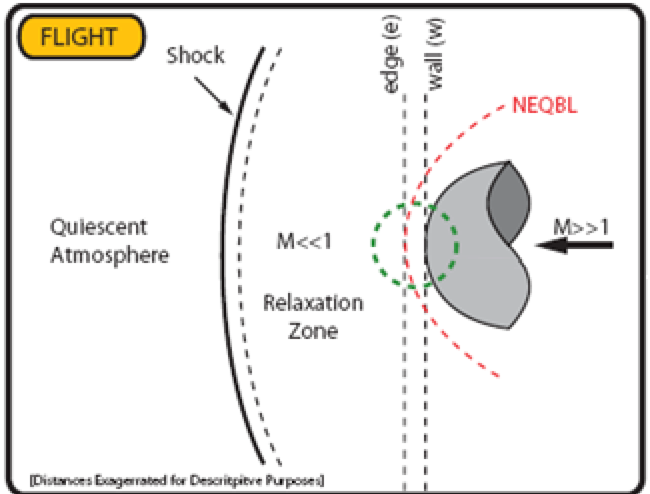
Micro-Architectured Surfaces

**Surface Catalysis at Extreme Environment**

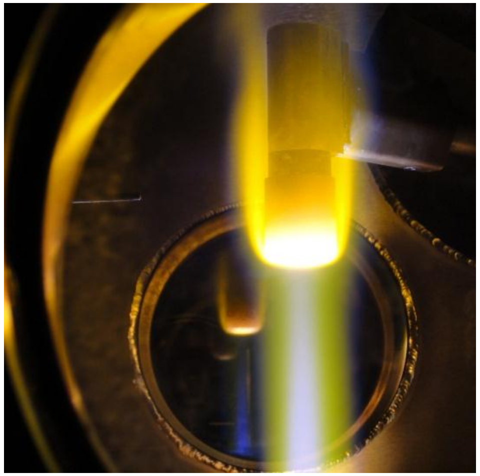
## III. Challenges, Motivations and New initiatives.

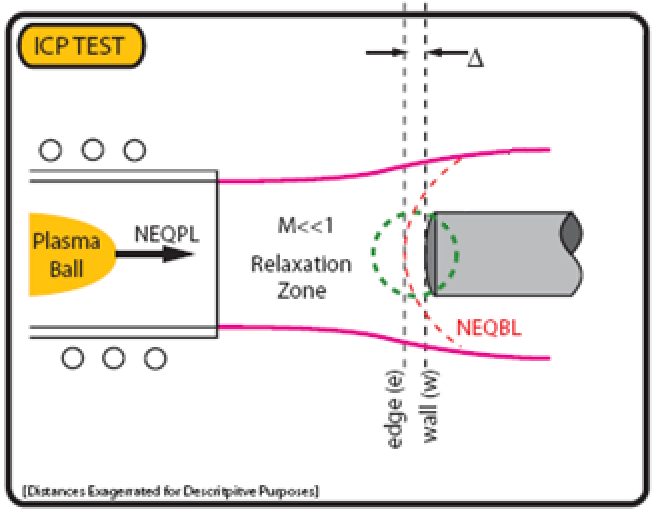
# Surface Catalysis Testing in a 30kW ICP Torch Facility

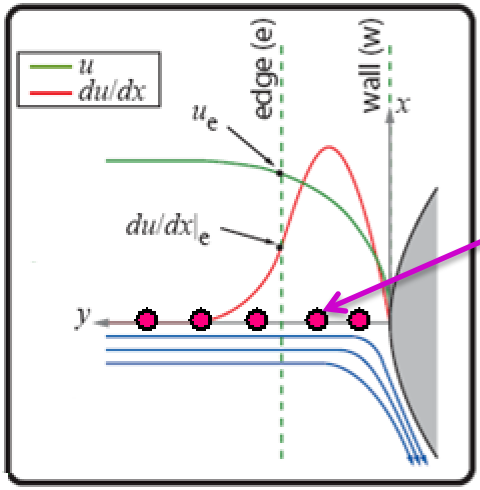
D. Fletcher (U. VERMONT), J. Marshall (SRI), M. Akinc (ISU), J. Prepezko (U. Wisconsin)




**Approach:** Compare surface-catalyzed reaction efficiencies for flexible and rigid materials with same elemental composition by measuring relative atom density and temperature gradients above material samples in the 30 kW ICP Torch Facility using laser induced fluorescence





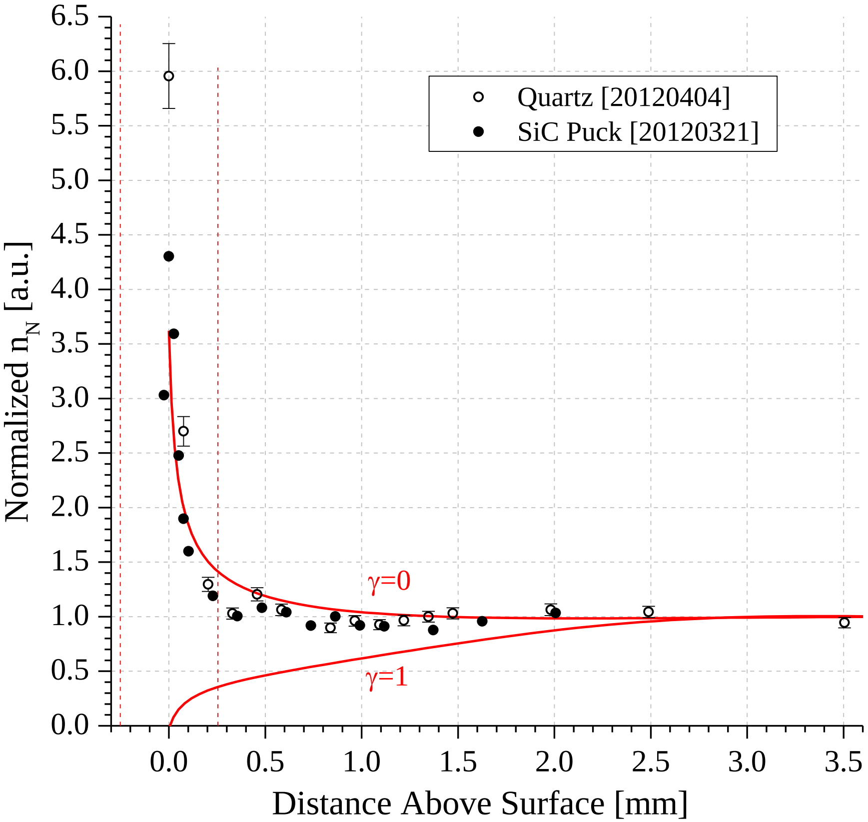

$$N + N + [s] \rightarrow [s] + N_2$$

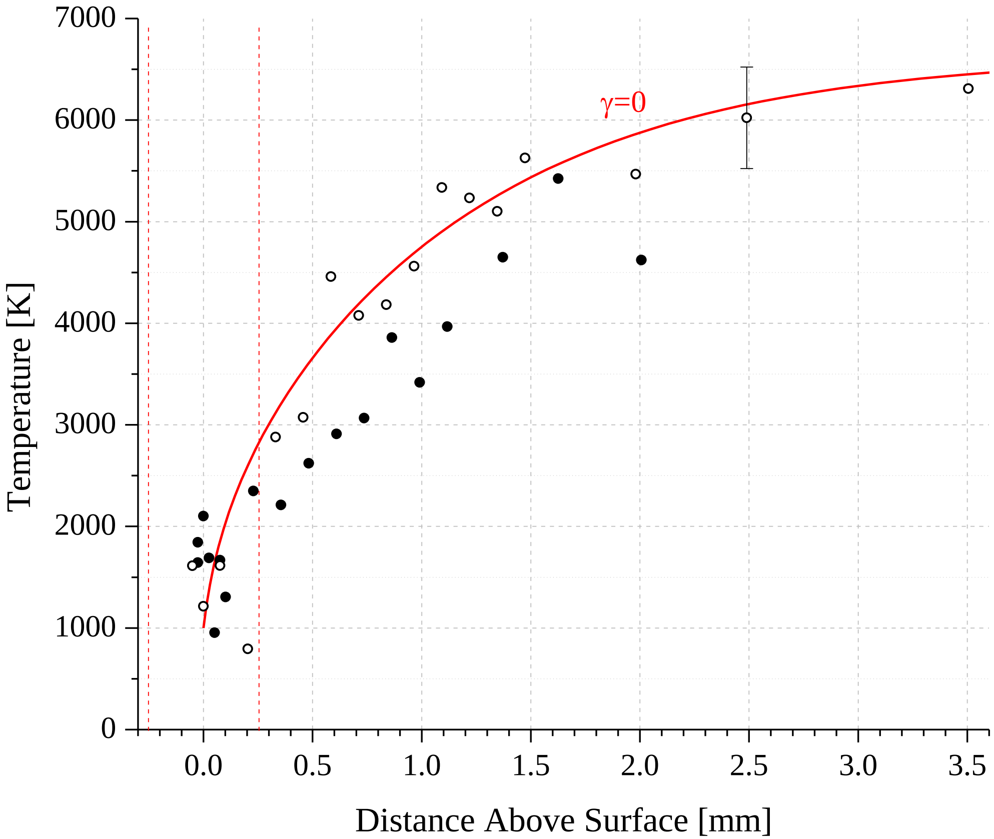
Spatially resolved measurement location

*Flight environment to ground facility testing comparison*

# Surface Catalytic Effect of SiC Testing in a 30kW ICP Torch Facility

D. Fletcher (U. VERMONT), J. Marshall (SRI), M. Akinc (ISU), J. Prepezko (U. Wisconsin)




- Relative N atom concentration measurements for quartz and monolithic $\alpha$-SiC
- Increasing concentration toward wall indicates low surface catalyzed reaction efficiency
- From the $n_N$ plot, it can be seen that $\alpha$-SiC ($T_w$ = 1300 K) is of comparable catalycity to quartz ($T_w$ < 1000 K)

# OUTLINE

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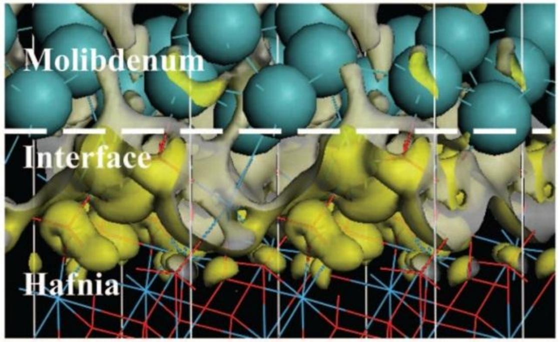
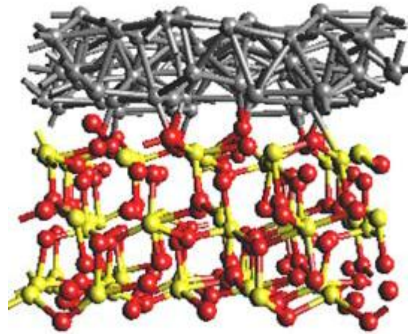
## III. Challenges, Motivations and New initiatives.

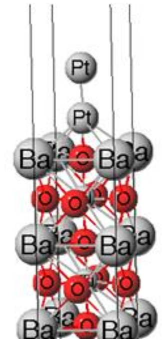
# 2012 BRI: 2D-Materials for Extreme Environments
# 2013 BRI: Charge Transfer at the Interface




Demkov 2010



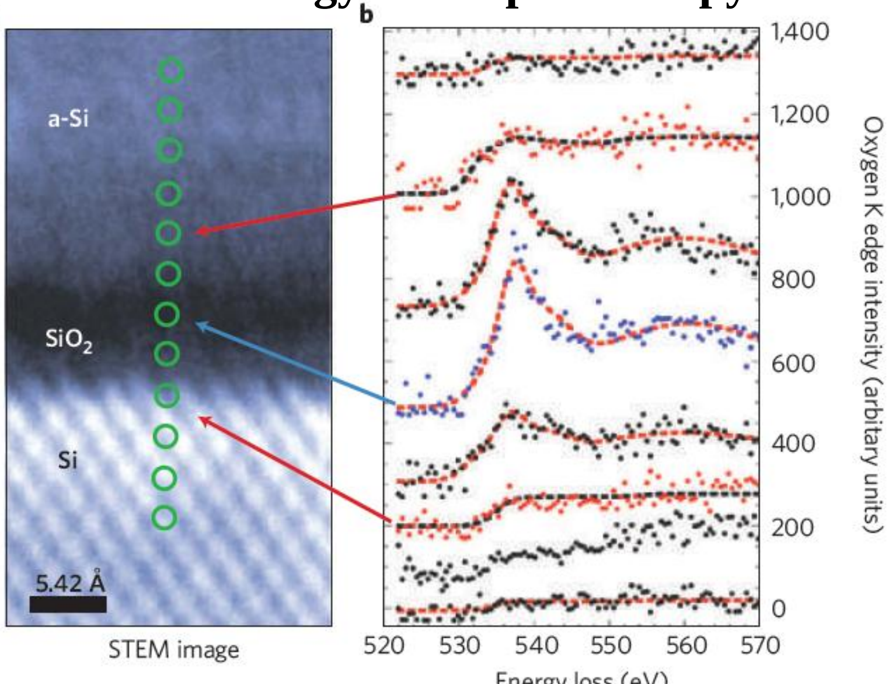
Inoue 2009



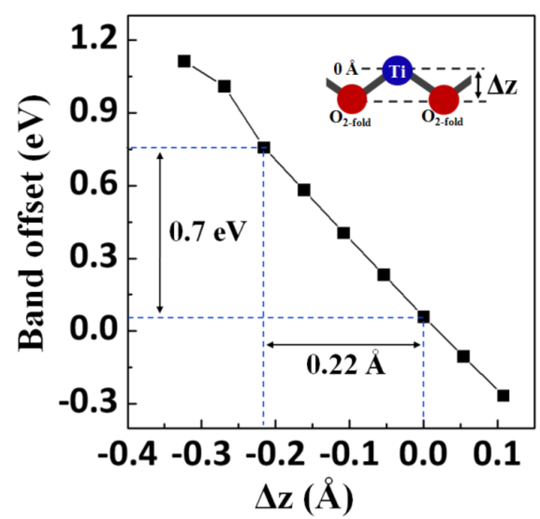

Heidger 2012

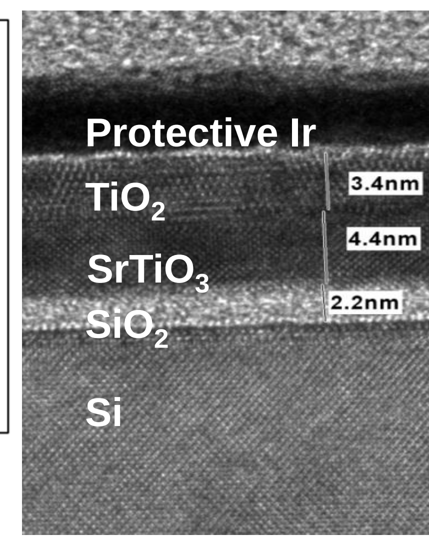
- Demkov: Diffuse Interface
- Inoue: Stoichimetyry of $Hf_{1-x}O_{2-\xi}$
- Heidger: Termination

## Electron Energy Loss Spectroscopy




## Interfacial dielectric response




A. Demkov, unpublished work

# SUMMARY

## I. Predictive Materials Science

Bulk Metallic Glasses
Carbides (SiC, TaC, $Ta_4C$)
Textile Based Hybrid Composite (NHSC)
**2012 MURI: Mosaic of Structure (CMU): Descriptor Challenge (wt. Dr. Fahroo)**
**2012 MURI: Atomic Scale Interface (LEHIGH) / (Dr. Shifler / ONR)**
**2013 MURI: Peridynamics (wt. Drs. Stargel & Fahroo)**

## II. Materials Far from Equilibrium

Micro-Architectured Surfaces
Surface Catalysis at Extreme Environments
**2013 BRI: Layered Structured Materials (2D E-Gas)**

## III. Challenges, Motivations and New initiatives

**2012 MURI: Template-Directed Directionally Solidified Eutectic Metamaterials**

**2013 MURI: Magneto-Electric Energy Conversion Materials and Terahertz Emission in Unbiased Dielectrics (wt. Dr. Luginsland)**

**2013 BRI: Metal Dielectric Interface: Charge Transfer in Heterogeneous Media under Extreme Environments (wt. Dr. Luginsland)**